ROCKFORD

ROCKFORD DIAMOND TECHNOLOGY, INC.

Professional Arts Building
501 S. Sixth Street, Suite 101
Champaign, IL 61820-5579
(217) 359-3569
(217) 356-2911 fax
email: rtainc@aol.com

February 23, 1995

Dr. John Pazik
Program Officer
Office of Naval Research
Ballston Tower One
800 North Quincy Street
Arlington, Virginia 22217-5660

RE: Rockford Diamond Technology, Inc., Contract No. N00014-94-C-0209

Dear Dr. Pazik:

Please find attached data requirement 0001AE - the fifth technical progress report. I am also enclosed the Material Inspection and Receiving Report (MIRR) DD Form 250. I am using the MIRR as an invoice for payment. I understand that if the report is acceptable at your destination, the consignee will forward the acceptance verification to the designated payment office. If I have filled the form out incorrectly or anything else, please give me a call.

Sincerely,

Lori Ballinger

Lori Ballinger
Business Manager
Rockford Diamond Technology, Inc.

cc:
Code S14031A; DCMAO Chicago; Attn: Andrea Kalb, Administrative contracting Officer, (CAO COPY - GCAS)
Code N00173; Director, Naval Research Laboratory; Attn: Code 2627
Code S47031; Defense Technical Information Center

Summary of Progress

Diamond growth in our microwave lamp has been successfully demonstrated. The samples grown for six hours show the crystalline structure with the grain sizes of 1~3 μm by an optical microscope. X-ray diffraction (XRD) also indicated these samples were diamond films with random orientation. However, bad samples with black appearance were also obtained sometime. By the Raman measurements, the black films were basically graphite. This phenomenon is strange since the growth conditions for the good and the bad samples were similar. It may be resulted from the change of plasma characteristics by adjusting the impedance. The experimental plan to demonstrate the UV enhancement of diamond growth in microwave plasma assisted CVD (MPACVD) is described in detail.

EXPERIMENTAL PLAN AND DETAILS

Figure 1 shows the experimental setup for the demonstration of UV enhanced diamond growth. The gas mixture consists of H_2, CH_4, Ar, and H_2O. H_2 and CH_4 are the basic species for diamond growth. Ar can also enhance the diamond growth by energy and charge transfer [Zhu et al. 1990]. In addition, argon excimers emit photons at 129 nm in microwave discharge. Water vapor introduced by a bubbler will be dissociated by the 129-nm photons and create additional energetic species (H and OH) to enhance the growth rate. The flow rates of hydrogen and methane is controlled by mass flow controllers while the rotameters are used to read and control the flow rates of argon and water.

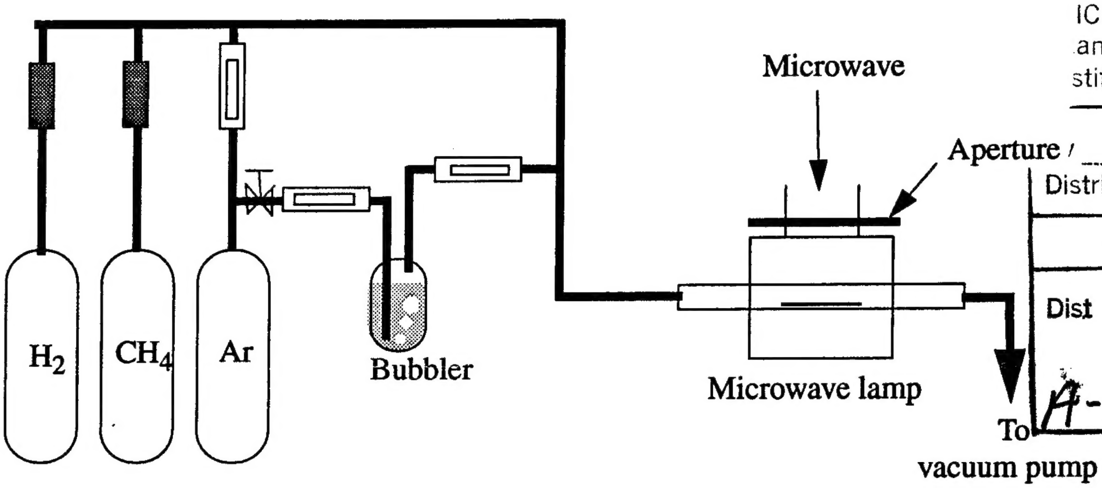

Figure 1. The experimental setup for the internal coupling method.

There are three stages for the demonstration of UV enhancement in a microwave lamp for diamond growth. First, we should demonstrate that good diamond films can be grown inside a microwave lamp with a gas mixture of H_2 and CH_4 by adjusting the microwave power and the methane concentration. The second step is to add argon into the gas phase to determine the optimal concen-

tration of argon. The total pressure should be kept the same since the plasma condition is mostly sensitive to the total gas pressure (while the growth rate is simply proportional to the concentration of the carbon carrier, methane). In the third stage, water vapor is introduced to study the effect of UV dissociation on diamond growth.

DIAMOND GROWTH IN A MICROWAVE LAMP

Several growths have been performed in the microwave lamp. Table 1 shows the growth condition for each samples. The pressure for all growths was 30 Torr. The actual power absorbed in the plasma is equal to the transmitted power (P_t) minus the reflected power (P_r) and the power absorbed by the structural material of the cavity and the waveguide (P_s, usually 30~80 W). The (111) silicon substrates were seeded by diamond powder (nanocrystals) (for sample 4 and 5) or prepared by scratching (for the others). It is difficult to measure the substrate temperature when the experiment is running since microwaves will interfere the temperature measurement. However, it can be indicated by the microwave power level due to the proportionality of the substrate temperature with the microwave power.

Table 1: Growth conditions of diamond samples

Sample	P_t (W)/P_r (W)	CH_4(%)	Growth time	Substrate position
4 6 7	700/130	1.5	6 hours	Center of the cavity 2.5 cm upstream to center 2.5 cm downstream to center
5 8 9	900/150	1.5	6 hours	Center of the cavity 2.5 cm upstream to center 2.5 cm downstream to center
10	700/100	1.2	12 hours	Center of the cavity
11	700/100	1.5	20 minutes	Center of the cavity
12 13 14	600/100	1.5	3 hours	Center of the cavity 2.5 cm upstream to center 2.5 cm downstream to center

These experiments tried to find the best microwave power level and the substrate position for the future experiments. Table 2 gives the analysis of the samples. The first two groups, sample 4 to 9, show the diamond crystalline structure with grain sizes of 1~3 μm. The grain sizes of sample 4 and 5 are slightly larger than the others. It is indicated that the substrates at the center of the cavity obtained the better films than those at other positions. In addition, the secondary nucleation was observed and there were some small clusters standing on the background film. The density of such

clusters on the samples grown at 900 W is higher than that on the samples grown at 700 W. XRD of these films show that the orientation of diamond structure is random. Also, sample 4 grown at 700 W is obviously better than sample 5 grown at 900 W. Sample 4 has been examined by Raman measurements (however, the spectrum is not available at the time of preparing the report). Two band with peaks around 1332 (not a very sharp peak) and 1519 cm^{-1} indicated the co-existence of diamond and diamond-like carbon (DLC).

Table 2: Results of growths

Sample	Appearance	Grain size	XRD	Raman
4 6 7	gray	~3 μm ~1 μm ~1 μm	Fig. 2 Fig. 3 -	diamond and DLC - -
5 8 9	gray	1~2 μm ~1 μm ~1 μm	Fig. 4 - Fig. 5	-
10	black	amorphous	-	-
11	black	amorphous	-	-
12 13 14	black	amorphous	-	-

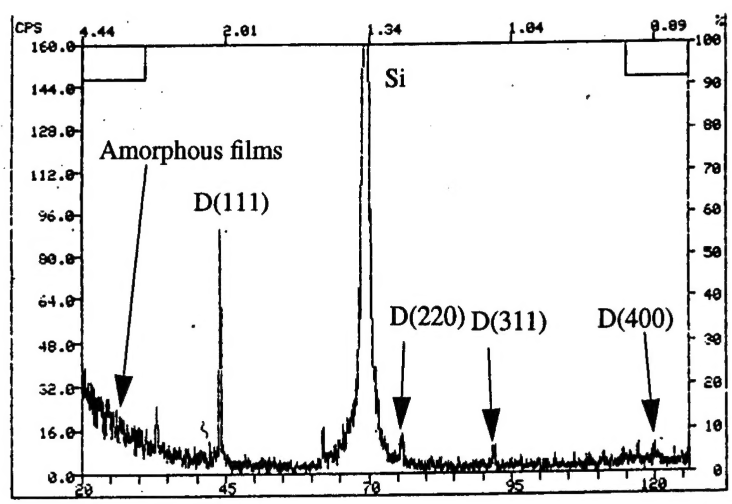

Figure 2. XRD of sample 4.

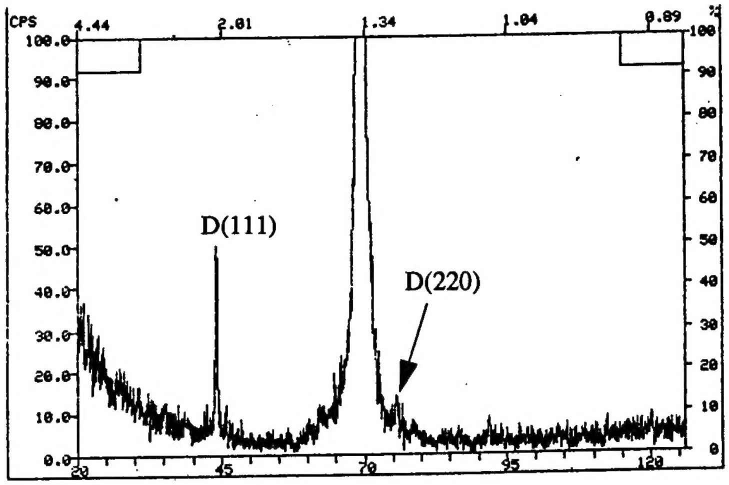

Figure 2. XRD of sample 6.

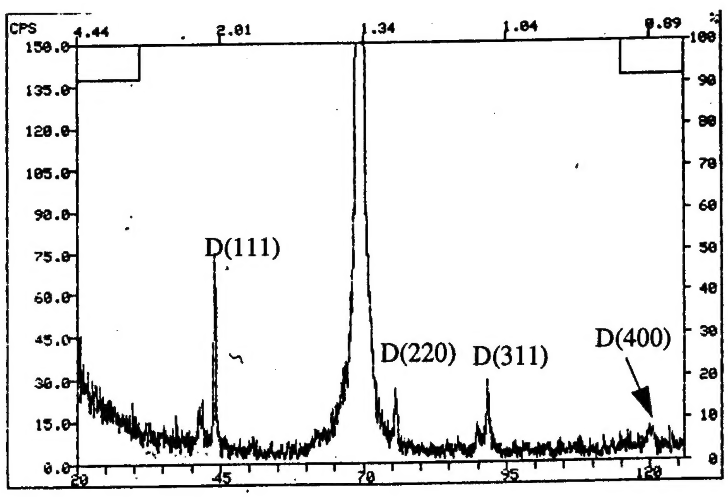

Figure 2. XRD of sample 5.

The other samples with black appearance show the complex of little shiny (or transparent) plates with black substance under the optical microscope. These films are similar to those we reported in December. It is strange that different results came from the same growth condition. This phenomenon might result from the change of the plasma characteristics while adjusting the system impedance and needs further verification. There was always a black coating inside the plasma tube when having these black films. Raman measurements showed this coating was graphite, which revealed the temperature of the tube was too high to grow diamond.

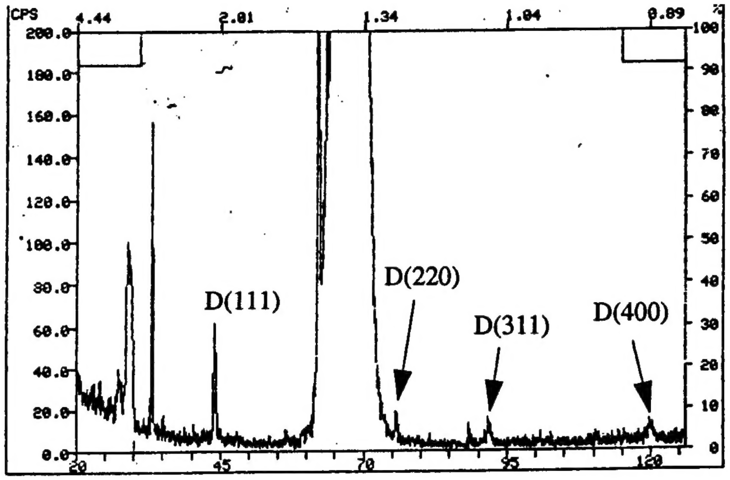

Figure 2. XRD of sample 9.

REFERENCES

Zhu, W., Inspektor, A., Badzian, A. R., McKenna, T. and Messier, R., *J. Appl. Phys.*, **68**(4), 1489-1496, (1990).

Plan for Next Month

A series of experiments for the internal coupling method will be performed with different argon and water concentrations. The aim is to prove the enhancement of diamond growth rate with UV photons. Thus, the photochemical method can be used in other applications. The external coupling method will also be examined. The UV intensity at the active region of a photo-CVD reactor will be evaluated theoretically.

OFFICE OF THE UNDER SECRETARY OF DEFENSE (ACQUISITION)
DEFENSE TECHNICAL INFORMATION CENTER
CAMERON STATION
ALEXANDRIA, VIRGINIA 22304-6145

IN REPLY REFER TO DTIC-OCC

SUBJECT: Distribution Statements on Technical Documents

TO:
OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

19951027 047

1. Reference: DoD Directive 5230.24, Distribution Statements on Technical Documents, 18 Mar 87.

2. The Defense Technical Information Center received the enclosed report (referenced below) which is not marked in accordance with the above reference.

TECHNICAL REPORT #5
N00014-94-C-0209
TITLE: ROCKFORD DIAMOND TECHNOLOGY

3. We request the appropriate distribution statement be assigned and the report returned to DTIC within 5 working days.

4. Approved distribution statements are listed on the reverse of this letter. If you have any questions regarding these statements, call DTIC's Cataloging Branch, (703) 274-6837.

FOR THE ADMINISTRATOR:

1 Encl

GOPALAKRISHNAN NAIR
Chief, Cataloging Branch

FL-171
Jul 93

DISTRIBUTION STATEMENT A:

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED

DISTRIBUTION STATEMENT B:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES ONLY; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT C:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND THEIR CONTRACTORS; (Indicate Reason and Date Below). OTHER REQUESTS FOR THIS DOCUMENT SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT D:

DISTRIBUTION AUTHORIZED TO DOD AND U.S. DOD CONTRACTORS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT E:

DISTRIBUTION AUTHORIZED TO DOD COMPONENTS ONLY; (Indicate Reason and Date Below). OTHER REQUESTS SHALL BE REFERRED TO (Indicate Controlling DoD Office Below).

DISTRIBUTION STATEMENT F:

FURTHER DISSEMINATION ONLY AS DIRECTED BY (Indicate Controlling DoD Office and Date Below) or HIGHER DOD AUTHORITY.

DISTRIBUTION STATEMENT X:

DISTRIBUTION AUTHORIZED TO U.S. GOVERNMENT AGENCIES AND PRIVATE INDIVIDUALS OR ENTERPRISES ELIGIBLE TO OBTAIN EXPORT-CONTROLLED TECHNICAL DATA IN ACCORDANCE WITH DOD DIRECTIVE 5230.25, WITHHOLDING OF UNCLASSIFIED TECHNICAL DATA FROM PUBLIC DISCLOSURE, 6 Nov 1984 (Indicate date of determination). CONTROLLING DOD OFFICE IS (Indicate Controlling DoD Office).

The cited documents has been reviewed by competent authority and the following distribution statement is hereby authorized.

A

(Statement)

OFFICE OF NAVAL RESEARCH
CORPORATE PROGRAMS DIVISION
ONR 353
800 NORTH QUINCY STREET
ARLINGTON, VA 22217-5660

(Controlling DoD Office Name)

(Reason)

(Controlling DoD Office Address, City, State, Zip)

Debra T. Hughes

DEBRA T. HUGHES
DEPUTY DIRECTOR
CORPORATE PROGRAMS OFFICE

(Signature & Typed Name)

(Assigning Office)

19 SEP 1995

(Date Statement Assigned)